LA-UR -89-2486

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

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LA-UR--89-2486

DE89 015345

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ATRAPT AND 'IPRG INTERNATIONAL CONFERENCE ON HIGH PRESSURE
SCIENCE AND TECHNOLOGY
JULY 1989
HIGH PRESSURE LABORATORY
UNIVERSITY PADERBORN
FEDERAL REPUBLIC OF GERMANY

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ABSTRACT

The recent discovery of a solid-solid phase change in shock-compressed Mo and the theoretical interpretation suggest valence d-electron density as a major influence on structural stability. The relationship of this experimental result to the transition metal structures and alloy phase diagrams will be discussed. Specific predictions will be presented for the locations and slopes of transition metal and transition metal alloy phase boundaries.

KEY WORDS

Transition metals, phase transition

A solid-solid phase transformation has recently been reported for Mo at high shock pressures (Hixson et al., 1989). This phase transition, detected by an abrupt change in elastic wave velocity of shock compressed Mo, has been interpreted in terms of the pressure-induced shift of conduction electrons from s-like states to d-like states (McMahan, 1986). Previous theoretical (McMahan, et al., 1981) and experimental (Brown et al., 1985) work on Lanthanum have shown that the gradual shift of s-like to d-like electrons can have large effects on the equation of state, particularly in the derivatives, Gruneisen's gamma and the bulk modulus.

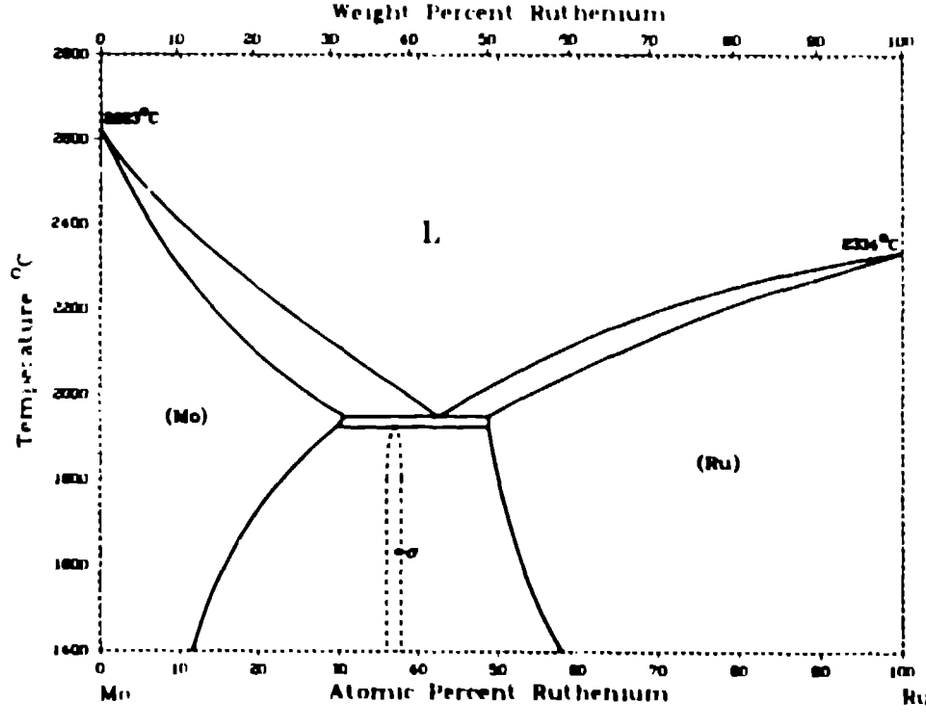
Skriver has shown through detailed LMTO calculations that the phase stability of the transition metals is dependent on the conduction d-electron density (Skriver, 1985). He shows that the stability of the bcc phase for group-V and VI transition metals at low temperature and pressure is dependent on having between 2.5 and 5 d-like electrons per ion. The group-VI metals Cr, Mo, and W need roughly 0.5 more d-electron per ion to cause stabilization of a close-packed phase, while the group-IV metals need only a small increase in d-electron occupancy to cause stabilization of the bcc phase.

In addition to pressure or increase in atomic number, another way to increase the d-electron occupation is by alloying with a higher-z metal. A phase diagram of the Mo-Ru system is shown in Fig. 1. The maximum ruthenium concentration in the bcc phase alloy is 30 atomic percent in the Mo rich component of the eutectic. The phase diagrams for Mo alloys with Tc, Ru, Rh, and Pd, as well as those for W alloys with Re, Os, Ir, and Pt are all similar (Massalski, 1986). We show the maximum solute concentrations in the bcc phase and the average number of electrons per ion in Table I. From this table we see that adding roughly 0.5 electron per ion to the Mo system and 0.4 electron per ion to the W system will destabilize the bcc lattice. These numbers are roughly consistent with Skriver's calculations.

Another recent calculation confirming the d electron occupation dependence of phase stability has been presented for Re (Watson et al., 1988). APW calculations show that as pressure is increased on Re causing the shift from s like to d like conduction electrons, the hcp phase remains stable in contrast to the suggestion that

* This work was supported by the U.S. Department of Energy.

there may be a high-pressure bcc phase. On the basis of the unhybridized band calculations one expects pressure to drive Re away from the region of stability for bcc



Mo-Ru Phase Diagram

At the high temperatures and pressures in a strong shock, phase stability calculations must include all the terms in the Gibbs free energy. In particular the phonon entropy term which stabilizes the bcc structure at high temperature is important (Animalu, 1967). The electron entropy term will be generally smaller so long as $T < 0.1\,T_F$, the Fermi temperature. Using a rigid band model, this term which is proportional to the density of states at the Fermi surface favors the bcc structure except for systems with six valence electrons per atom (Morazzi, 1978). The other term in the free energy differences, PAV, will also become important at sufficiently high pressures. Another complication in the very high pressure phase diagram is the hybridization of the s and d bands at pressures high enough that all valence electrons behave s like. We expect again to stabilize the bcc lattice (Hoover et al., 1972).

Table I

Alloy	Atomic % Solute	Conduction Electrons Per Ion
Mo-Tc	50	6.5
Mo-Ru	30	6.6
Mo-Rh	20	6.6
Mo-Pd	7	6.3
W-Re	37	6.4
W-Os	19	6.4
W-Ir	10	6.3
W-Pt	5	6.2

We have shown that experiment and theory consistently suggest that d-electron occupation plays a dominant role in crystal structure stability and thermodynamics of transition metals. These observations suggest several more theoretical and experimental tests of the underlying physics. We know, for example that the hcp-bcc boundary for the group-IV elements, Ti, Zr, and Hf has a negative dP/dT. This suggests that pressure stabilizes the bcc phase along an isotherm, consistent with the increase in d-band occupancy. However, the other terms in the Gibbs free energy should be evaluated to show whether this phenomenon is really d-electron determined. Also, since alloying and pressure appear to have the same effect on structural stability by alloying Mo with Ru or W with Re, for example, one should force the bcc-hcp phase boundary to lower pressures, where it may be accessible to techniques other than strong shock loading.

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